HEXAVALENT CHROMIUM PAPER – GROUNDWATER RESOURCES ASSOCIATION OF CALIFORNIA TECHNICAL COMMITTEE

The environmental impact of Cr(VI) is a controversial issue critical to the protection of groundwater resources. The Erin Brokovich movie highlighted the need to understand and protect drinking water sources from contamination by hexavalent chromium (Cr(VI)). In the spring of 2001, the Groundwater Resources Association of California (GRA) developed a hexavalent chromium symposium where experts discussed the science, regulatory policies and legal issues associated with this controversial pollutant. The following summary of facts and issues was prepared by the GRA Technical Committee to promote rational discussion and assist in sound groundwater policy implementation. A reference list is also attached.

• PERSISTENCE IN GROUNDWATER: Sampling of groundwater in California and other states has shown that Cr(VI) can exist as chromate and dichromate in groundwater. The speciation of chromium in groundwater is governed by pH and Eh. Cr(VI) can exist naturally in groundwater that has been unaffected by local industrial activity. At least one hypothesis is that naturally occurring fluoride forms a soluble complex with Cr(III)-bearing minerals, after which the dissolved Cr(III) contacts with MnO_2-containing aquifer material, causing oxidation to Cr(VI). Cr(VI) in groundwater can be reduced to Cr(III) at low pH and under reducing conditions. The reduced form of chromium [Cr(III)] can be oxidized by manganese (IV) oxide and oxygen.

• TASTE AND ODOR: There is no perceptible odor or taste that chromium imparts to water.

• HEALTH RISK: Cr(VI) is considered a suspected carcinogen. Some scientists suggest that Cr(VI) can cause cancer when inhaled as a vapor, as through showering, but disagreements exist over safe limits of Cr(VI) when ingested as potable water. As with all toxic substances particularly metals exposure through inhalation has the highest risk. However, the only way for Cr(VI) to be inhaled is if a person is exposed to chromium fumes or if Cr(VI) in airborne soil / water droplets (aerosols) is inhaled.

FATE AND TRANSPORT: Cr(VI) is a chemical that has been used in paint pigments, chrome plating, other manufacturing processes such as leather tanning, used by the aircraft and other industries for anodising aluminium, the refractory industry uses chromite for forming bricks and shapes, as it has a high melting point, moderate thermal expansion, and stable crystalline structure.

Cr(VI) is rapidly reduced to Cr(III) when ferrous iron (Fe-II) or manganese (Mn-II) are present in chemically-reduced groundwater. There have been several examples of this immobilization phenomenon, both in industrial situations here in the US, and at a chromium chemicals plant in Poland. Recent work on isotopic ratios of Cr(VI) may prove useful in evaluating the source or distance traveled, and possibly whether Cr(VI) is natural or anthropogenic in origin.

• GROUNDWATER INVESTIGATION: The investigation of a groundwater resource impacted with Cr(VI) requires analysis of groundwater for both Cr(VI) and total chromium. Analytical methods used include the USEPA method for drinking water EPA 218.6. The equivalent method for wastewater (used for contaminated groundwater as well) is SW 7196A or 7199. Method 7199 is the more sensitive method with a low detection limit of 0.02 ug/l of Cr(VI). This method uses ion chromatography to estimate Cr(VI). Total chromium is analysed using ICP-MS using methods SW-6010 or 6020. While analyzing for chromium, it is important to monitor interferences such as sulfide, vanadium, molybdenum, organic carbon. This will ensure greater reliability and validity of analytical data.

• REMEDIATION: Cr(VI) can be remediated in-situ by a variety of technologies including but not limited to sulfur based treatment technologies. Calcium polysulfide added to the soil and groundwater reduces Cr(VI) to trivalent chromium (Cr(III) which is precipated as chromium hydroxide, a non-toxic, low solubility form of chromium. Other methods to remediate hexavalent chromium include the reduction of Fe(III) in the aquifer material to Fe(II) using sodium dithionate. The Fe(II) then reduces Cr(VI) to Cr(III). In situ microbial reduction of Cr(VI) is also possible both under aerobic and anaerobic conditions. In both these processes, Cr(VI) is reduced to Cr(III) which is then precipitated as Cr(OH)3 and immobilized in the aquifer matrix.

Phytoremediation is a way for selected plants to incorporate the hexavalent chromium into their cell structures, effectively removing it from the shallow soil.

Extraction technologies, such as pump and treat systems have been used to remove the Cr(VI) from the subsurface and treat the chemical with above ground systems, including but not limited to, reduction by ferrous iron compounds followed by alkaline precipitation, ion exchange with regenerant treatment or disposal, electrochemical reduction followed by alkaline precipitation (in which ferrous iron forms electrochemically, instead of being added as a purchased chemical), and acidic reduction at pH <3.0 with sulfur dioxide, sodium sulfite, sodium bisulfite, or sodium metabisulfite. (Reduction with sulfite-containing chemicals is not normally selected for a number of practical reasons, including which is the greater potential for incomplete conversion of the Cr(VI) to Cr(III).

• Cr(VI)-SPECIFIC REGULATORY GUIDELINES:

Neither the federal or state government limit Cr(VI) in water, but both regulate total chromium, instead. The federal government has a cap of 100 ug/L for total chromium. California limits the total chromium in drinking water to 50 ug/L. There is no MCL for Cr(VI). The California Office of Environmental Health Hazard Assessment recommended a PHG (Public Health Goal of 2.5 ug/L for total chromium and 0.02 ug/L for Cr(VI). The OEHHA has rescinded the PHG and the

State is working at establishing an MCL for Cr(VI) (for more details see the DHS website)

• RECOMMENDATIONS: The characteristics of Cr(VI) in the subsurface make assessment and remediation of Cr(VI)-impacted sites complicated and difficult to delineate spacially, especially considering the potential occurrence of natural Cr(VI) that has not yet been characterized. Therefore, competent environmental professionals should be used in the assessment and remediation of Cr(VI) impacted soil and groundwater resources. The GRA Board urges continued state and federal legislative support for three areas:

1. establishing a reliable, accurate analytical method for Cr(VI) estimation;

2. optimizing an effective ex situ treatment system for Cr(VI) in groundwater (this is important because unlike industrial wastewater, Cr(VI) in several drinking water sources is in trace levels and therefore more difficult to treat effectively and efficiently.); and

3. evaluation of the health risks posed by low levels of Cr(VI), if any, and establishment of actual background levels in natural groundwater (accompanied by health effect studies) before reacting with new regulations that are unsupported by proper scientific evaluation.

The GRA Technical Committee prepared this document. GRA is a multi-disciplinary professional organization dedicated to the study and protection of groundwater resources.

REFERENCES

General Health Risks

1. California Dept. of Health Services
   http://www.dhs.ca.gov/ps/ddwem/chemicals/Chromium6/Cr+6index.htm_

This is the DHS webpage on chromium in drinking water. It has very useful links to chromium concentrations in drinking water in the State, the PHG document and the rationale behind rescinding the PHG for chromium (total and hexavalent)

2. AWWARF is supporting a study on treatment of chromium in drinking water. See this link for papers
http://www.mcguireinc.com/papers.html

Cr(VI) and Groundwater Resources

3. The USGS is conducting a background chromium study in the Mojave Desert. They propose to use stable isotope ratio analysis to determine the natural and anthropogenic sources of chromium. See http://wwwbrr.cr.usgs.gov/projects/GWC_chemtherm/chromium.htm for an abstract of the study.

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